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ARIMITSU KOJI

(54) BASE PROPAGATOR, BASE PROPAGATOR COMPOSITION, REACTIVE BASE COMPOSITION AND PATTERN FORMING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a base propagator which is decomposed by the action of a base and forms a new base and to obtain a composition containing the base propagator.

SOLUTION: The base propagator comprises a urethane compound containing at least one urethane bond. The urethane compound is decomposed by the action of a base derived from an amino group forming the urethane bond and generates a base derived from the urethane bond. The base propagator composition consists of the base propagator and a base generating agent. A photosensitive composition consisting of the base propagator, a photo-base generating agent and a polymerizable epoxy compound is prepared and used as a pattern forming material to form the objective pattern.

LEGAL STATUS

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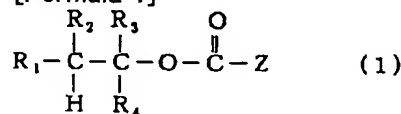
CLAIMS

[Claim(s)]

[Claim 1] It is the base growth agent characterized by consisting of an urethane system compound containing at least one urethane bond, and for an operation of the base of the amino-group origin which forms this urethane bond decomposing this urethane system compound, and generating the base of this urethane bond origin.

[Claim 2] This urethane system compound is the following general formula (1).

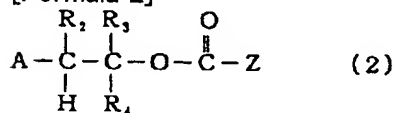
[Formula 1]



It is the base growth agent of claim 1 which is the urethane system compound expressed with (one of these shows an electronic suction nature machine, R3 and R4 show hydrogen or a substituent, and Z shows the amino group at least although R1 and R2 show hydrogen, a substituent, or an electronic suction nature machine among a formula).

[Claim 3] This urethane system compound is the following general formula (2).

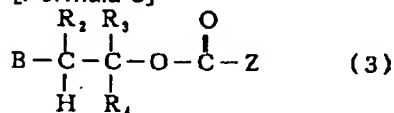
[Formula 2]



It is claim 1 or the base growth agent of 2 which is the urethane system compound expressed with (A shows a fluorenyl group among a formula, R2 shows hydrogen or a substituent, R3 and R4 show hydrogen or a substituent, and Z shows the amino group).

[Claim 4] This urethane system compound is the following general formula (3).

[Formula 3]



It is claim 1 or the base growth agent of 2 which is the urethane system compound expressed with (B shows an organic sulfoxide radical among a formula, R2 shows hydrogen or a substituent, R3 and R4 show hydrogen or a substituent, and Z shows the amino group).

[Claim 5] The base growth agent constituent characterized by consisting of one of the base growth agents and base generating agents of claims 1-4.

[Claim 6] The constituent of claim 5 with which a base generating agent consists of a compound which generates a base with heating.

[Claim 7] The constituent of claim 5 with which a base generating agent consists of a compound which generates a base by the exposure of an activity energy line.

[Claim 8] The base reactivity constituent characterized by consisting of one of the base growth agents, the base generating agents, and the base active substance of claims 1-4.

[Claim 9] The constituent of claim 8 with which a base generating agent consists of a compound which generates a base by the exposure of heating or an activity energy line.

[Claim 10] The photosensitive constituent which consists of one of the base growth agents, the optical base generating agents, and polymerization nature epoxy compounds of claims 1-4.

[Claim 11] The pattern formation approach characterized by using the photosensitive constituent of claim 10 as a pattern formation ingredient.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the base growth agent and base growth agent constituent which generate a base according to an operation of a base, a base reactivity constituent, a photosensitive constituent, and the pattern formation approach.

[0002]

[Description of the Prior Art] It is put in practical use in many fields that the chemical structural change produced according to an operation of actinic rays, such as light, infrared radiation, far infrared rays, an electron ray, or an X-ray, is used for the resin sensed for actinic rays or its constituent as an image formation ingredient, or it uses hardening of a monomer or a prepolymer for surface coating processing etc. Although it is the light which is widely used among actinic rays and actinic rays are hereafter specified and explained to light, the actinic rays to the resin of this invention or its constituent are not limited to light. The sensitization rate in these resin or its constituent, a sensitization wavelength field, and definition are various, these suitable properties are chosen according to the purpose, and the photopolymer or constituent suitable for it is chosen. However, the essential trouble as follows existed, respectively. Although the photopolymer which uses polymeric materials as a principal component reaches far and wide as a photosensitive ingredient in which it is mass-produced and high definition is shown and it came to be used (refer to Yamaoka, edited by Nagamatsu, "photopolymer technology", and Nikkan Kogyo Shimbun (1988)), in order to shorten the time amount required for forming an image and a pattern, maintaining the outstanding definition, development of the further photosensitive high sensitivity ingredient is desired.

[0003] In order to raise the sensitization rate of the photopolymer ingredient for image formation, various attempts have so far been made. But it is the photopolymerization system to which having been widely set as the object of development carries out the polymerization of many vinyl monomers continuously by making into an initiator the radical kind generated in an operation of light. Moreover, the cationic polymerization system which is made to generate an acid in an operation of light and makes this acid a catalyst is also the object of active development. Since these polymerization reactions carry out induction of the chemical change of the low-molecular matter which carried out dissolution distribution into the high polymer itself or a macromolecule, they can use for image formation physical-properties change produced as a result. However, in the case of a radical polymerization, since a polymerization reaction is checked by the oxygen in air, by the thin film system, the special device for oxygen cutoff is needed especially. The configuration of the relief pattern form since it be neutralize by the minute amount alkali to which the strong acid generate from a photo-oxide generating agent exist in an environment by optical exposure, although it be advantageous be spoil at the point which, on the other hand, do not have such oxygen inhibition effectiveness by the optical cationic polymerization system, and the problem that definition fall in cost price be point out in the field of the micro or the resist ingredient for nano lithography.

[0004] On the other hand, practical use is widely presented with the technique of stiffening resin according to an operation of light and a quantum line for a short time, as what realizes high-

speed processing of a surface coating object and a non-solvent surface treatment process. Although the radical polymerization is broadly utilized also for this purpose, the inhibition effectiveness by the oxygen in air must be taken into consideration. With the hardening technique of using cationic polymerization, although it was advantageous since there was no inhibition effectiveness of oxygen, problems by the strong acid as an initiator, such as corrosion and the denaturation of resin, remained. Moreover, practical use is similarly presented with the hybrid mold-curing technique which combined the exposure and heat treatment by light or the electron ray widely as what realizes high-speed processing of a surface coating object and a non-solvent manufacture process. Furthermore, although the sensible-heat hardening resin constituent of 1 acidity or alkalinity which took in the principle which generates an acid and a base thermally potentially was also widely set as the object of examination, it looked forward to all performing hardening in a heat treatment process more quickly from a viewpoint of energy saving.

[0005] Using the polymerization reaction and chemical reaction by the base catalyst as one method of conquering such a trouble is proposed. For example, there is the approach of making generate the amine as a base and carrying out chemistry denaturation of the resin by making this into a catalyst according to an operation of light and heat. It is applicable to image formation using a soluble change before and after chemistry denaturation. However, the generating effectiveness of the base generated in an operation of light has come to have sufficient sensibility practical from a low thing etc. On the other hand, since the resin which has an epoxy group causes crosslinking reaction by operation of a base and it stiffens an epoxy resin, it generates the amines as an initiator or a catalyst within an epoxy system resin layer according to an operation of light and heat, and, subsequently there is [the approach of stiffening by heat-treatment etc.]. However, in this case, since the engine performance of the ingredient which can be hardened according to an operation of light and an electron ray is low, practical use has come to be presented with it.

[0006] Thus, in order to high-performance-ize further the **** formation and the hardening technique based on a radical kind, a cation kind, the polymerization reaction further started with a base kind, or a chemical reaction, the inhibition effectiveness by the oxygen in air is not received, but excluding a staining substance like the strong acid to generate, it is still more efficient and a resin constituent with which a reaction advances is desired strongly.

[0007] In catalytic reaction, in order that the number of the catalyst molecules which involve there may not change, according to a certain poisoning operation, a catalyst deactivates and a reaction stops it. Or catalytic reaction stops also by controlling diffusion in a solid-state strongly. Therefore, what is necessary is just to make the number of the molecules which have a catalysis increase in process of catalytic reaction, in order to make catalytic reaction make it efficient further. Namely, what is necessary is to decompose in autocatalysis and just to find out the matter which generates the molecule which newly has catalyst ability. It decomposes in [actually until now] autocatalysis, strong acid is generated, and the acid growth reaction which has the property that the concentration of strong acid increases nonlinearly is proposed (Arimitsu, Ichimura, the high sensitivity organic system light image formation ingredient incorporating a growth reaction, a functional material, 17 (12), 16 -24 (1997) reference). Thus, the acid growth agent which an acid increases in growth is found out, and the resin constituent with which high performance-ization is attained is also known by adding them (KArimitsu, KKudo and KIchimura, J.Am.Chem.Soc., 120, 37 -45 (1998) reference).

[0008]

[Problem(s) to be Solved by the Invention] This invention makes it the technical problem to offer the pattern formation approach using the photosensitive constituent while offering the base growth agent which decomposes itself and generates a new base according to an operation of a base, a base growth agent constituent, a base reactivity constituent, and a photosensitive constituent.

[0009]

[Means for Solving the Problem] this invention person came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. That is,

according to this invention, it consists of an urethane system compound containing at least one urethane bond, and the base growth agent characterized by for an operation of the base of the amino-group origin which forms this urethane bond decomposing, and this urethane system compound generating the base of this urethane bond origin is offered. Moreover, according to this invention, the base growth agent constituent characterized by consisting of said base growth agent and a base generating agent is offered. Furthermore, according to this invention, the base reactivity constituent characterized by consisting of said base growth agent, a base generating agent, and the base active substance is offered. According to this invention, the photosensitive constituent characterized by consisting of a base growth agent, an optical base generating agent, and a polymerization nature epoxy compound is offered further again. According to this invention, the pattern formation approach characterized by using said photosensitive constituent as a pattern formation ingredient is offered further again.

[0010]

[Embodiment of the Invention] When the base growth agent of this invention makes the same base as the base which decomposes according to an operation of a base, and generates a base, and is generated in this case act, it has the property of decomposing and generating a base. Therefore, the base of the equivalent smaller than it is made to only act to the constant rate, it decomposes in self-multiplication, finally the whole quantity decomposes, and the base growth agent of this invention generates a lot of bases corresponding to the base growth dose.

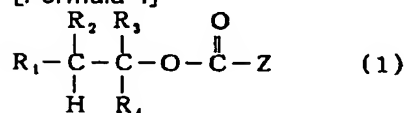
[0011] The base growth agent of this invention consists of an urethane system compound which has said property. That is, the base growth agent of this invention consists of an urethane system compound containing at least one urethane bond, an operation of the base (ammonia or amine) of the amino-group origin which forms this urethane bond decomposes this urethane system compound, and it is characterized by generating the base (ammonia or amine) of this urethane bond origin. Of course, even if it makes a different base from the base of the amino-group origin which forms the urethane bond act, it decomposes and a base is generated.

[0012] Until now, although various kinds of urethane system compounds are known, there is nothing that has been recognized as a base growth agent. It can be judged by the easy preliminary experiment shown below whether the urethane system compound has a function as a base growth agent.

(Base growth diagnosis) the base HNR one R2 same to the amino group NR one R2 which forms the urethane bond (—OCONR one R2) of the urethane system compound in the 2wt% methanol-d4 solution of an urethane system compound as the base of the origin — 0.1wt(s)% — after putting the added solution into NMR spectrum test sample tubing and carrying out the sealed tube of this, it heats at 100 degrees C and an NMR spectrum is measured. By the increment in the NMR signal of the olefin generated by disassembly of an urethane compound, an urethane system compound is judged to be what has a base growth function.

[0013] Generally the base growth agent of this invention consists of an urethane system compound expressed with the following general formula (1).

[Formula 4]



R1 and R2 are hydrogen, a substituent, or an electronic suction nature machine among said formula, and at least one of these is an electronic suction nature machine. R3 and R4 are hydrogen or a substituent, and Z is an amino group.

[0014] In organic electron theory etc., the electronic suction nature machine of common use, for example, a fluorenyl group, an organic sulfoxide radical, a cyano group, a nitro group, an ester group, a carbonyl group, an amide group, a pyridyl radical, etc. are included by said electronic suction nature machine.

[0015] What is expressed with the following general formula (4) is included by said organic sulfoxide radical.

[Formula 5]

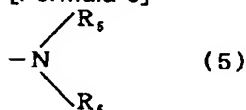


the inside of said formula, and Ar -- an organic radical -- it is an aryl group preferably. Phenyl, tolyl, naphthyl, etc. are mentioned as the example. the carbon number of Ar -- 6-18 -- it is 6-12 preferably.

[0016] said substituent -- carbon numbers 1-12 -- desirable -- the alkyl group of 1-6, and carbon numbers 5-10 -- desirable -- the cycloalkyl radical of 6-8, and carbon numbers 6-14 -- desirable -- the aryl group of 6-10, and carbon numbers 7-15 -- the arylated alkyl radical of 7-11 etc. is included preferably. As the example, methyl, ethyl, propyl, butyl, cyclohexyl, phenyl, tolyl, naphthyl, benzyl, phenethyl, naphthyl methyl, etc. are mentioned.

[0017] The non-permuted amino group and the permutation amino group are included by said amino group. The mono-permutation amino group and the JI permutation amino group are included by the permutation amino group. Said amino group can be expressed with the following general formula (5).

[Formula 6]

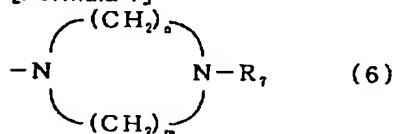


[0018] R5 and R6 show hydrogen or an organic radical among said formula. the carbon number of an organic radical -- 1-18 -- it is 6-12 preferably. An alkyl group, a cycloalkyl radical, an aryl group, and an arylated alkyl radical are included by this organic radical. as an alkyl group -- especially -- carbon numbers 1-12 -- the thing of 2-6, for example, ethyl, propyl, butyl, hexyl, etc. are mentioned preferably. as a cycloalkyl radical -- carbon numbers 5-10 -- the thing of 6-8, for example, cyclohexyl, cyclo octyl, etc. are mentioned preferably. as an aryl group -- carbon numbers 6-14 -- the thing of 6-10, for example, phenyl, tolyl, naphthyl, etc. are mentioned preferably. as an arylated alkyl radical -- a carbon number -- 7-15 -- the thing of 7-11, for example, benzyl, phenethyl, naphthyl methyl, etc. are mentioned preferably. Said alkyl group, the cycloalkyl radical, the aryl group, and the arylated alkyl radical may have the substituent. As a substituent in this case, the amino group, an alkoxy group, an alkoxy carbonyl group, an acyl group, an acyloxy radical, a hydroxy group, etc. are mentioned.

[0019] In the amino group of said general formula (5), R5 and R6 can be connected and they can form a nitrogen ring. the number of annular atoms of the nitrogen ring in this case -- 3-12 -- it is 5-8 preferably. Moreover, said nitrogen ring can contain two or more hetero atoms (N, O, S, etc.) in the annular atoms.

[0020] In this invention, what is expressed with the following general formula (6) can be mentioned as a desirable thing as said amino group.

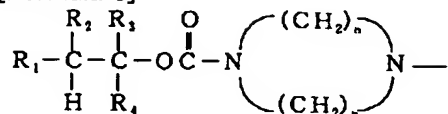
[Formula 7]



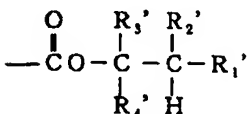
[0021] the inside of said formula, and n and m -- 1-6 -- the number of 2-4 is shown preferably. n+m -- 4-12 -- it is 4-8 preferably. Although R7 shows substituents, such as a hydrocarbon group besides hydrogen, a hydrocarbon oxy-radical, and an acyl group, it may be residue of an urethane system compound which has a base growth function. the carbon number of the hydrocarbon group in the hydrocarbon group in a hydrocarbon group and a hydrocarbon oxy-radical, and an acyl group -- 1-12 -- it is 1-8 preferably. Alkyl, cycloalkyl, aryl, and arylated alkyl are included by this hydrocarbon group.

[0022] The urethane system compound used as a base growth agent of this invention can contain two or the urethane bond beyond it. As such an urethane system compound, what is expressed with the following general formula (7) and (8) can be mentioned.

[Formula 8]

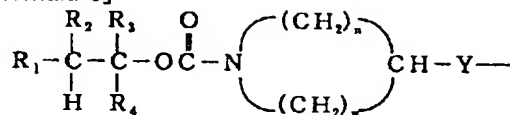


(7)

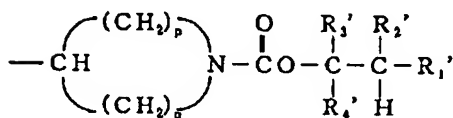


[0023]

[Formula 9]



(8)



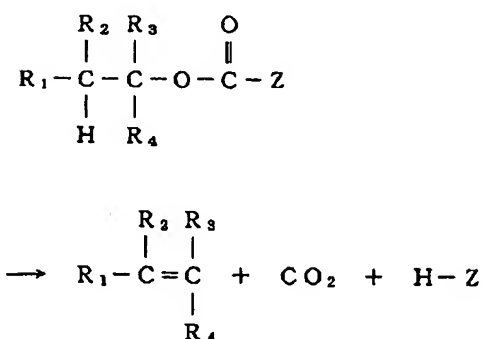
[0024] In said general formula (7), R1 and R2 are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R3 and R4 are hydrogen or a substituent. R1' and R2' are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R3' and R4' are hydrogen or a substituent. n and m -- 1-6 -- the number of 2-4 is shown preferably. n+m -- 4-12 -- it is 4-8 preferably.

[0025] In said general formula (8), R1 and R2 are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R3 and R4 are hydrogen or a substituent. R1' and R2' are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R3' and R4' are hydrogen or a substituent. Y -- carbon numbers 1-8 -- it is the alkylene group of 2-6 preferably. n and m -- 1-6 -- the number of 2-4 is shown preferably. n+m -- 4-12 -- it is 4-8 preferably. p and q -- 1-6 -- the number of 2-4 is shown preferably. p+q -- 4-12 -- it is 4-8 preferably.

[0026] As an example of said electronic suction nature machine and a substituent, what was shown in connection with said general formula (1) can be illustrated.

[0027] The base growth agent of this invention is characterized by the electronic suction nature machine and the hydrogen atom having combined with the carbon atom contiguous to the carbon atom which contains a urethane bond and the urethane group (carbamoyl group) combines on the molecular structure. Therefore, the hydrogen atom combined with the carbon atom which the electronic suction nature machine has combined for such a structural description is tintured with an acid-property, and drawing is possible for it by operation of a base. If the mechanism of the base growth reaction by the base growth agent of this invention is shown, first, drawing of said hydrogen atom will happen according to an operation of a base, subsequently carbamic acid will ****, this will decompose further, and a base and a carbon dioxide will be generated. And the base generated on this occasion acts on other base growth agent molecules, that molecule is made to disassemble, and a base is generated. Thus, it is decomposed in chain reaction and a base growth agent can generate a lot of bases by a small amount of base after all. It is as follows when a reaction formula shows said base growth reaction taking the case of the urethane system compound of said general formula (1).

[Formula 10]

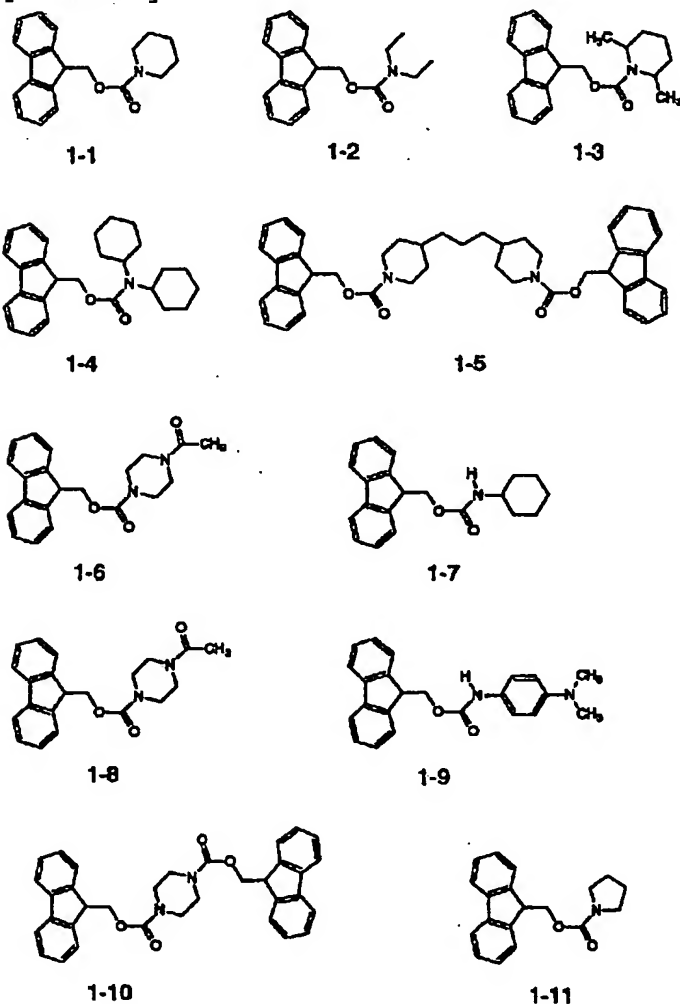


The base of the amino-group origin which H-Z in said reaction formula has combined with the urethane bond is shown. this base — ammonia — or it is an amine preferably. What is necessary is to make chloro formate react to alcohol, to generate asymmetric carbonic acid diester and just to make a base react subsequently to this carbonic acid diester, in order to prepare the base growth agent of this invention.

[0028] The example of the base growth agent of this invention is shown below.

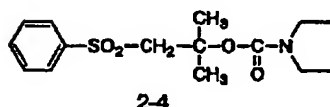
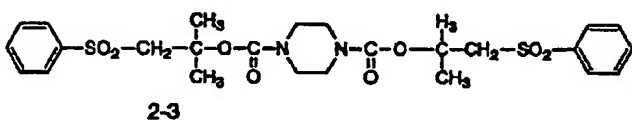
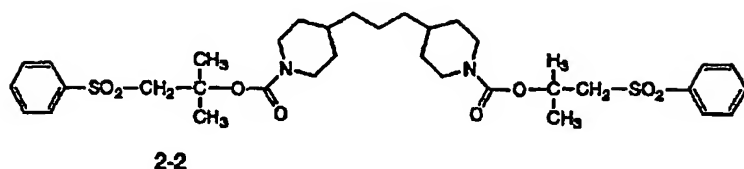
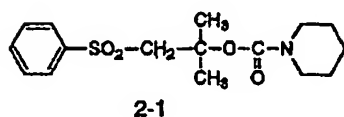
[0029]

[Formula 11]



[0030]

[Formula 12]



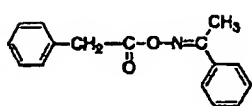
[0031] Said compound of No.1-1-1-11 shows the example of the fluorene system base growth agent which the fluorenyl group has combined as an electronic suction nature machine, and generates an amine in growth. On the other hand, said compound of No.2-1-2-4 shows the example of the sulfone system base growth agent which the organic sulfoxide radical has combined as an electronic suction nature machine, and generates an amine in growth.

[0032] The base growth agent of this invention is thermally stable at a room temperature, and can be saved over a long period of time. if little addition of the base which dissolves this base growth agent into an organic solvent, and triggers early catalytic reaction in this is carried out and it carries out a pyrogenetic reaction — from specific reaction time — rapid — decomposition — happening — SIG — the reaction curve which consists of a MOIDARU curve is given, and it can check that the base growth reaction is advancing from now on.

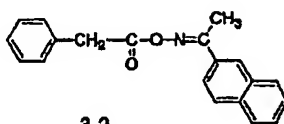
[0033] The base growth agent constituent of this invention is a constituent containing a base growth agent and a base generating agent. This constituent can have the shape of liquefied or a solid-state. What generates a base with heating, the thing which generates a base by the exposure of activity energy lines (electromagnetic waves, electron rays, etc., such as light and an X-ray) are included by the base generating agent. Conventionally, such a base generating agent is well-known, and can use various kinds of things. For example, as a base generating agent which generates a base according to an operation of light, what is used for a chemistry magnification mold photoresist is used ("imaging business the volume on owner ** electronics ingredient research community, organic material", the **** exudation version (refer to 1993)). Moreover, in order to expand the sensitization wavelength field of these optical base generating agents, a photosensitizer can also be made to live together suitably. With the photoreaction nature matter, the base generated by the photolysis of these matter acts on a base growth agent, and promotes generating of a base. The optical base generating agent preferably used for this invention below is illustrated.

[0034]

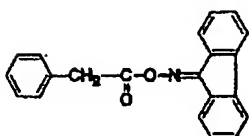
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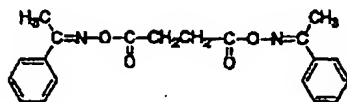
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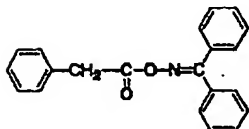
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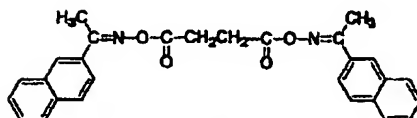
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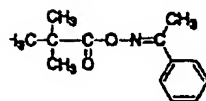
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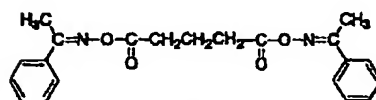
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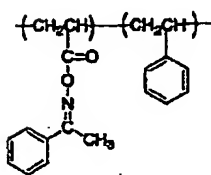
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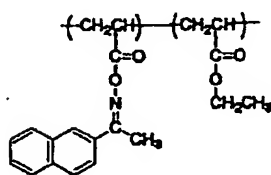
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3-8



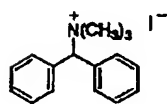
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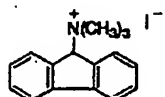
3-10

[0035]

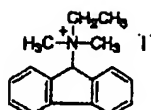
[Formula 14]



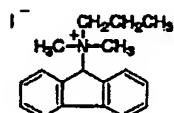
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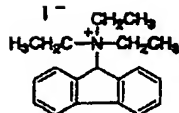
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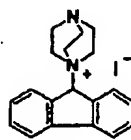
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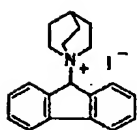
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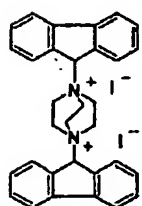
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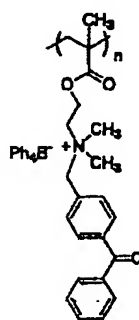
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4-7



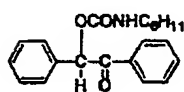
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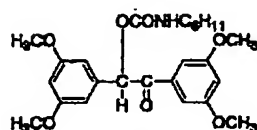
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[0036]

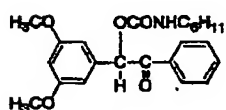
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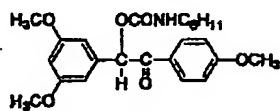
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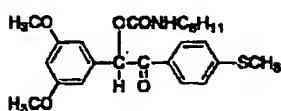
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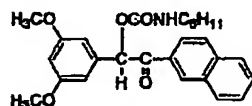
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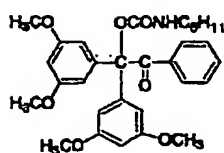
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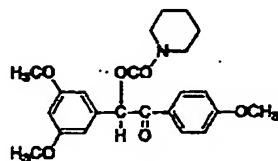
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5-6



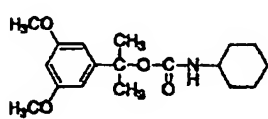
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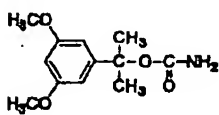
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[0037]

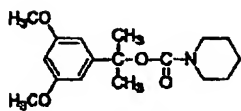
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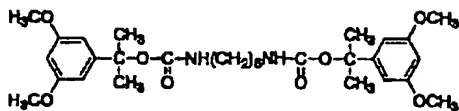
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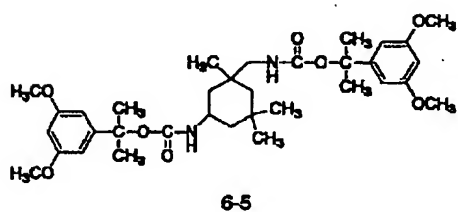
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6-3



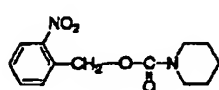
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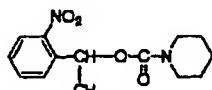
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[0038]

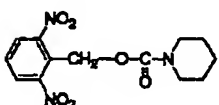
[Formula 17]



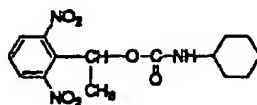
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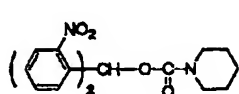
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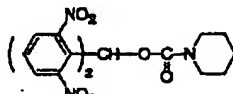
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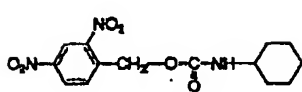
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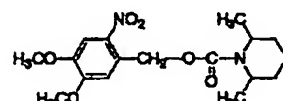
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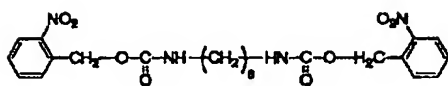
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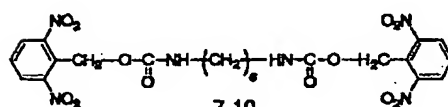
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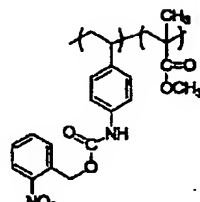
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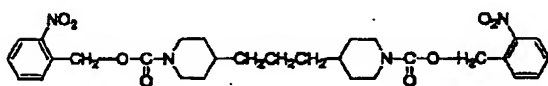
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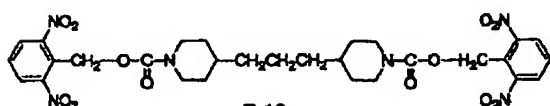
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7-11



7-12



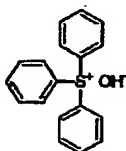
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[0039]

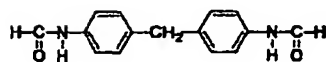
[Formula 18]



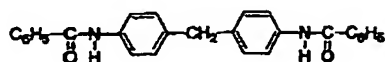
8-1



8-2



8-3



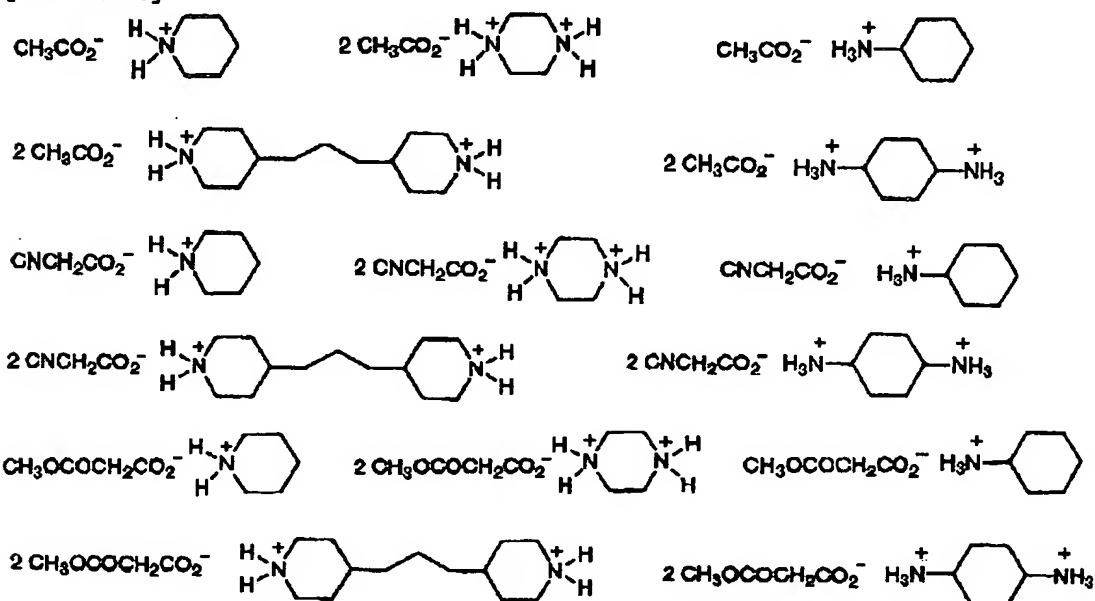
8-4

[0040] Said compound of No.3-1-No.3-10 is an oxime ester system compound, generates a

Schiff base according to an operation of light, and generates an amine by this hydrolysis. Here, the compound of No.3-9 and No.3-10 is a high molecular compound, and generates an amine by the optical exposure to the macromolecule side chain. The compound of No.4-1-No.4-9 is an ammonium system compound, and generates the third class amine by the photolysis. The compound of No.5-1-No.5-8 is a benzoin system compound, and generates an amine by the photolysis. The compound of No.6-1-No.6-5 is a dimethoxy benzyl urethane system compound, and generates an amine by the photolysis. The compound of No.7-1-No.7-13 is an alt.nitrobenzyl urethane system compound, and generates an amine by the photolysis. Other optical base generating agents are shown in No.8-1-No.8-4. The compound of No.8-1 generates ammonia as a base by the exposure of light. The compound of No.8-2 generates hydroxide ion as a base by the exposure of light. The compound of No.8-3 generates an amine as a base by the exposure of light. The compound of No.8-4 generates an amine as a base by the exposure of light. As a compound which generates a base with heating, the following can be shown, for example.

[0041]

[Formula 19]

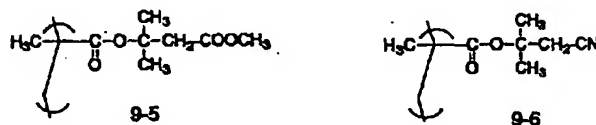
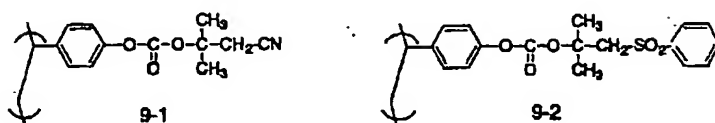


[0042] In the base growth agent constituent containing the base growth agent and base generating agent by this invention, although especially the rate of the base generating agent is not restrained, it is a weight ratio to a base growth agent, and is usually 5 - 40 % of the weight preferably one to 100% of the weight. Said base growth agent constituent generates the base in growth according to an operation of heat, light, etc. This constituent can make the reaction of that base active substance start by heating or optical exposure by blending this with various kinds of base active substance.

[0043] The base reactivity constituent of this invention is a constituent containing the base active substance, a base growth agent, and a base generating agent. This constituent can have the shape of liquefied or a solid-state. One sort or two sorts or more of chemicals which occur chemical reactions, such as a decomposition reaction, and an elimination reaction, a condensation reaction, a polymerization reaction, are included according to an operation of a base by the base active substance. This chemical can be the low-molecular matter, oligomer, a high polymer (polymer), etc. The base active substance can be a high polymer permuted by the residue which causes a base catalyst reaction, and can be the resin constituent or polymer which shows a condensation reaction by the base catalyst. Those examples are shown below.

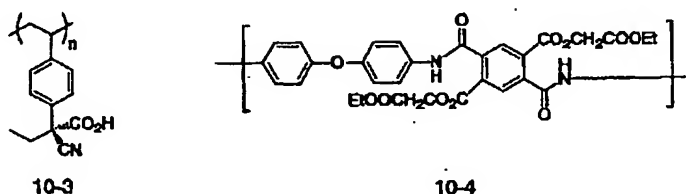
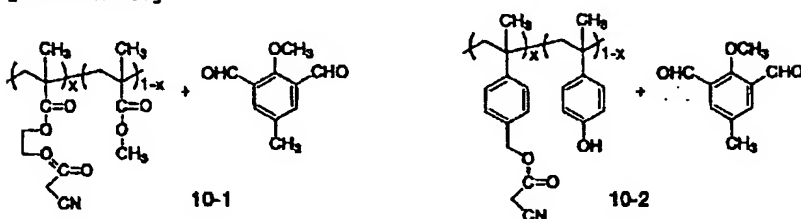
[0044]

[Formula 20]



[0045]

[Formula 21]

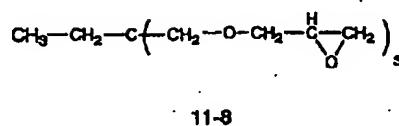
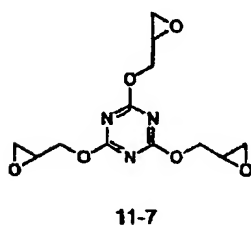
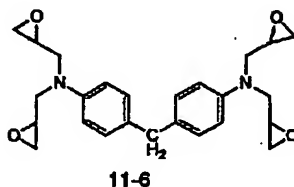
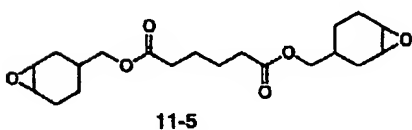
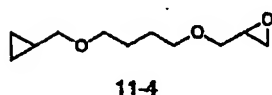
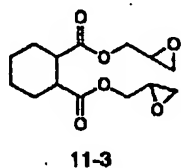
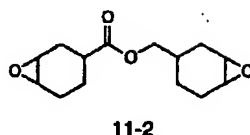
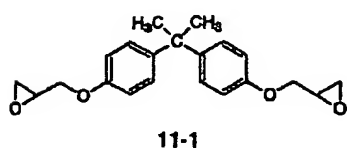


[0046] The compound of No.9-1-No.9-4 produces the reaction of desorption and a decarboxylation according to an operation of a base among said high molecular compounds of No.9-1-No.9-6. The compound of No.9-5 and No.9-6 produces the reaction of a decarboxylation according to an operation of a base. The matter (mixture) of No.10-1 produces the reaction of dehydration condensation and bridge formation according to an operation of a base among said base active substance of No.10-1-No.10-4. The matter (mixture) of No.10-2 produces the reaction of dehydration condensation and bridge formation according to an operation of a base. The matter (polymer) of No.10-3 produces the reaction of a decarboxylation according to an operation of a base. The matter of No.10-4 produces the reaction of imide formation according to an operation of a base.

[0047] The base active substance can be matter which has at least one epoxy group. By making a base (amine) act on the compound which has at least two epoxy groups, the epoxy compound can be made into a polymer by the ring opening polymerization of the epoxy group. Moreover, chemistry denaturation of the epoxy compound can be carried out by carrying out the addition reaction of the amine to an epoxy compound. The example of an epoxy compound which shows polymerization reactivity is shown below.

[0048]

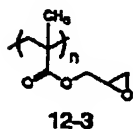
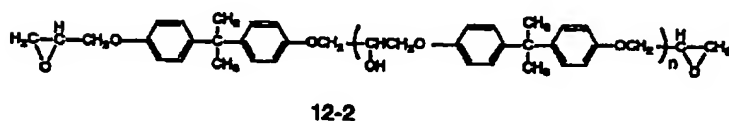
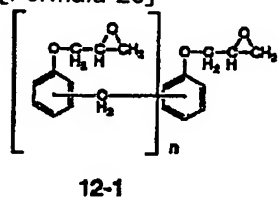
[Formula 22]



[0049] The example of other epoxy compounds (epoxy resin) in which polymerization reactivity is shown is shown below.

[0050]

[Formula 23]



[0051] In said base reactivity constituent, the rate of a base growth agent is usually about 2 – 30 % of the weight preferably one to 60% of the weight to the base active substance. When there are too few loadings of a base growth agent, it becomes impossible to make the base active substance react quickly. On the other hand, if many [too], the amount of the base generating agent used will increase, and the base generating agent itself will have big effect on the solubility of the base active substance, and it is disadvantageous in price. A base generating agent is good

to specify to 2 - 15% of the weight of within the limits especially preferably one to 20% of the weight to the base active substance.

[0052] The desirable base reactivity constituent by this invention is a polymerization reactivity constituent containing a polymerization nature epoxy compound. According to an operation of light or heat, the polymerization of such a constituent is carried out and it gives a polymer.

[0053] The desirable base reactivity constituent by this invention is a constituent which starts a polymerization reaction by light. This constituent is a constituent which consists of a polymerization nature epoxy compound, a base growth agent, and an optical base generating agent, and contains auxiliary components, such as a curing agent for polymerization nature epoxy compounds, and a hardening accelerator, other bulking agents, if needed. This constituent is advantageously used as a pattern formation ingredient. In order to form a pattern using this photosensitive constituent, this photosensitive constituent is dissolved in an organic solvent, coating liquid is made, this coating liquid is applied to the solid-state front face where a substrate etc. is suitable, it dries and a paint film is formed. To this paint film, pattern exposure is performed and a base is generated. Subsequently, it heat-treats and a chain of decomposition of a base growth agent is urged, although the conditions of heat-treatment are changed according to the class of base growth agent [activity / base / exposure energy and / to be used], the class of epoxy compound, etc. -- whenever [stoving temperature] -- the range of 60 to 150 degrees -- it is the range of 80 to 130 degrees more preferably. Heating time is 5 minutes from 30 seconds more preferably from 10 seconds for 10 minutes. Negatives are developed by immersing this into the solvent which produces a difference in solubility in the exposure section and the unexposed section, and a pattern is obtained.

[0054]

[Example] Next, this invention is explained in full detail according to an example.

[0055] Example 19-fluorenyl methyl chloroformate 2.00g was dissolved in ether 50ml, and the ether solution of one to 31 g HIPERIJIN was dropped at this under ice-cooling. After stirring at a room temperature for 20 minutes under ice-cooling for 1.5 hours, the reaction solution was washed in order of water, 5% hydrochloric acid, and saturation brine, and the organic layer was dried with sulfuric anhydride magnesium. The solid-state obtained by carrying out solvent distilling off was recrystallized in ethanol, and 0.98g N-(9-fluorenyl methyloxy carbonyl) piperidine (No.1-1) was obtained as a white crystal.

[0056] 47% melting point of 98-101 degrees C 1 H-NMR (90MHzCDCl₃) delta (ppm):1.55 (brs, 6H, CH₂) of yield, 3.3-3.6 (m, 4H, CH₂), 4.1-4.5 (m, 3H, CH, CH₂), 7.1-7.7 (m, 8H, Ar-H)
IR(KBr)(cm⁻¹):2936,1686,1437,1259,1232,1151,1106,762,739.

Calculated value as C₂₀H₂₁NO₂: C, 78.14;H, 6.89;N, 4.56%. Analysis value: C, 77.90;H, 6.72;N, 4.41%.

[0057] Like example 2 example 1, 9-fluorenyl methyl chloroformate was made to react with diethylamine, the column chromatography (bulking agent; silica gel (WAKOGERU C-200), expansion solvent; hexane:ethyl-acetate =20:1) refined the obtained product, and the 1.97g 9-fluorenyl methyl N-diethyl carbamate (No.1-2) was obtained as a colorless liquid.

[0058] 86.4% 1 H-NMR (90MHz, CDCl₃) delta (ppm):1.04 (t,Hz [J= 7.2], 4H, CH₂) of yield, 4.1-4.5 (m, 3H, CH, CH₂), 7.1-7.9 (m, 8H, Ar-H)

IR(neat)(cm⁻¹):2974,1696,1478,1451,1426,1273,1168,757,739.

Calculated value as C₁₉H₂₁O₂N: C, 77.25;H, 7.17;N, 4.74%. Analysis value: C, 76.92;H, 7.18;N, 4.80%.

[0059] By the same actuation as example 3 example 1, 9-fluorenyl methyl chloroformate was made to react with cis-2 and 6-dimethyl piperidine, the column chromatography (bulking agent; silica gel (WAKOGERU C-200), expansion solvent; hexane:ethyl-acetate =20:1) refined the obtained product, and 2.25g N-(9-fluorenyl methyloxy carbonyl)-cis-2 and 6-dimethyl piperidine (No.1-3) was obtained as a white crystal.

[0060] 86.9% melting point 80of yield -82degree-C1H-NMR(90MHz, CDCl₃) delta(ppm): — 1.10 (s, 3H, CH₃), 1.19 (s, 3H, CH₃), 1.3-1.9 (m, 6H, CH₂), and 7.1-7.9 (m, 8H, Ar-H)

IR(KBr)(cm⁻¹):2944,1703,1447,1409,1307,1085,763,738.

Calculated value as C₂₂H₂₅NO₂: C, 78.77;H, 7.51;N, 4.18%. Analysis value: C, 78.84;H, 7.57;N,

4.14%.

[0061] By the same actuation as example 4 example 1, 9-fluorenyl methyl chloroformate was made to react with dicyclohexylamine, the obtained solid-state was recrystallized in ethanol, and the 9-fluorenyl methyl N-dicyclohexyl KARUPA mate (No.1-4) was obtained as a white crystal.

[0062] 71.5% melting point of 190-194 degrees C 1 H-NMR (90MHz, CDCl₃) delta (ppm):0.5-2.0 (m, 22H, CH₂) of yield, 4.20 (t, J= 4.6Hz, 1H, CH) and 4.62 (d, J= 4.6Hz, 2H, CH₂O), 7.1-7.9 (m, 8H, Ar-H)

IR(KBr)(cm⁻¹):2926,1674,1441,1290,1238,1167,1119,1046,744.

Calculated value as C₂₇H₃₃NO₂: C, 80.37;H, 8.24;N, 3.47%. Analysis value: C, 80.56;H, 8.32;N, 3.42%.

[0063] 9-fluorenyl methyl chloroformate is made to react with a 1 and 3-G 4-piperidyl propane by the same actuation as example 5 example 1. the oil of the shape of an acquired starch syrup -- a column chromatography (bulking agent; -- silica gel (WAKOGERU C-200) --) expansion solvent; -- hexane: -- it refined by ethyl-acetate =2:1 and 9.10g 4 and 4'-[screw [(9-fluorenyl methyl) oxy-] carbonyl] trimethylene] dipiperidine (No.1-5) was obtained as a white crystal.

[0064] 36.0% melting point of 109 degrees C 1 H-NMR (90MHz, CDCl₃) delta (ppm):0.8-1.9 (m, 16H, CH, CH₂) of yield, 2.5-3.0 (br, 4H, N-CH₂), 3.9-4.5 (m, 10H, CH, CH₂O, N-CH₂), 7.1-7.9 (m, 16H, Ar-H)

IR(KBr)(cm⁻¹):2918,1695,1432,1217,1146,1103,759,741.

Calculated value as C₄₃H₄₆N₂O₄: C, 78.86;H, 7.08;N, 4.28%. Analysis value: C, 78.93;H, 7.21;N, 4.20%.

[0065] It is 1 and 1 in 10ml of example 6 N,N-dimethylacetamide. - It added to the solution which added dimethyl-2-(phenyl sulfonyl) ethyl p-nitrophenyl carbo NATO 1.50g (3.95mmol) and 1-hydroxy benzotriazol 0.162g (0.120mmol), stirring the piperidine 1.36g (16.0mmol) solution which dissolved in 10ml of N,N-dimethylacetamide at a room temperature. The reaction solution was stirred at 50 degrees C with the room temperature for 3 hours for 6 hours. This reaction solution was poured out into 400ml of 1% sodium-hydrogencarbonate water solutions, the generated precipitate was filtered, and it washed with water. Precipitate was dissolved in the ether, reduced pressure distilling off of the solvent was carried out after desiccation with sulfuric anhydride magnesium, and 0.91g N-[1 and 1-dimethyl-2-(phenyl sulfonyl) ethoxycarbonyl] piperidine (No.2-1) was obtained as a white crystal.

[0066] 70.0% melting point [of yield]: -- 104-105-degree-C1 H-NMR(90MHz, CDCl₃) delta (ppm):1.43- 1.55 (br, 6H, N-CH₂, CH₂), 1.67 (s, 6H, CH₃), and 3.1-3.3(m,4H,N-CH₂),3.89(s,2H,CH₂),7.3-8.0(m,5H,Ar-H).

IR(KBr)(cm⁻¹):1689(C=O),1310(SO₂),1143(SO₂)

Calculated value as C₁₆H₂₃O₄NS: C, 59.05;H, 7.12;N, 4.31;S, 9.85%. Analysis value: C, 59.07;H, 6.95;N, 4.30;S, 9.89%.

[0067] By the same actuation as example 7 example 6, it is 1 and 1-dimethyl -2 (phenyl sulfonyl) ethyl p. -Phenyl carbo NATO and a 1 and 3-G 4-piperidyl propane were made to react 2 fatty tuna, and the column chromatography (bulking agent; silica gel (WAKOGERU C-200), expansion solvent; hexane:ethyl-acetate =2:1) refined the obtained solid-state. The product was dissolved in chloroform, it refined by the reprecipitating method using a hexane, and 1.93g 4 and 4'-[screw [[1[1 and]-dimethyl-2-(phenyl sulfonyl) ethyl oxy-] Carbonyl] trimethylene] dipiperidine (No.2-2) was obtained as a white crystal.

[0068] yield: -- 53.0% melting point: -- 139-140-degree-C1 H-NMR (90MHz, CDCl₃) delta (ppm):1.14-1.80 (m, 28H, CH₃, CH₂, CH), 2.40-2.69 (br, 4H, N-CH₂), 3.76-4.04 (m, 8H, N-CH₂, SO₂CH₂), and 7.4-8.0 (m, 10H, Ar-H)

IR(KBr)(cm⁻¹):1688(C=O),1318(SO₂),1214(SO₂)

Calculated value as C₃₅H₅₀O₈N₂S₂: C, 60.84;H, 7.29;N, 4.06;S, 9.28%. Analysis value: C, 60.56;H, 7.05;N, 4.06;S, 8.75%.

[0069] Example 8 Pori (glycidyl methacrylate) and the cyclohexanone solution which contains 4 and 4'-[screw [(2-nitrobenzyl) oxy-] Carbonyl] trimethylene] dipiperidine (7-12) which is a 10wt (s)% optical base generating agent to this polymer were prepared. this solution -- the base growth agent 4 and 4'-[screw [(9-fluorenyl methyl) oxy-] carbonyl] trimethylene] dipiperidine

(No.1-5) — a polymer — receiving — 43wt(s)% — it added and considered as the solution of a photosensitive constituent. Spin spreading of this solution was carried out on silicon UNIHA on 1000rpm and the conditions for 30 seconds, and it prebaked by heating for 1 minute at 100 degrees C. After carrying out UV irradiation to this paint film, it heated for 15 minutes at 100 degrees C, and postbake processing was performed. Furthermore, it was immersed in 2-methoxy ethyl acetate for 30 seconds, and this film was developed. It washed and dried by ethanol, thickness was measured, and the sensitivity curve was searched for. Consequently, it turned out by adding a base growth agent that sensibility of single figure improves rather than the system under base growth agent un-existing. Moreover, after carrying out UV irradiation of the film which carried out spin spreading over the photo mask, the clear negative-mold image was obtained by washing of 2-methoxy ethyl acetate.

[0070] 2-methoxy ethyl acetate solution containing 4 and 4'-[screw-[[[(2-nitrobenzyl) oxy-] Carbonyl] trimethylene] dipiperidine (7-12) which is example 9 Pori (glycidyl methacrylate) and a 10wt% optical base generating agent was prepared. this solution — the base growth agent 4 and 4'-[screw [[[(1 and 1-dimethyl -2 (phenyl sulfonyl) ethyl) oxy-] carbonyl] trimethylene] dipiperidine (No.2-2) — a polymer — receiving — 20wt(s)% — it added and considered as the solution of a photosensitive constituent. Spin spreading of this solution was carried out on the silicon wafer on 1000rpm and the conditions for 30 seconds, and it prebaked by heating for 1 minute at 110 degrees C. After irradiating ultraviolet rays at this paint film, it heated for 15 minutes at 110 degrees C, and postbake processing was performed. Furthermore, it was immersed in 2-methoxy ethyl acetate for 30 seconds, and this film was developed. It washed and dried by ethanol, thickness was measured, and the sensitivity curve was searched for. Consequently, it turned out by adding a base growth agent that sensibility improves also 4 times rather than the system under base growth agent un-existing. Moreover, after carrying out UV irradiation of the film which carried out spin spreading over the photo mask, the clear negative-mold image was obtained by washing of 2-methoxy ethyl acetate.

[0071]

[Effect of the Invention] (1) Since the sensibility of the photosensitive constituent containing the base growth agent of this invention improves sharply, it can be used for a high sensitivity image formation ingredient.

(2) Since the yield of a base increases sharply by the base growth agent, it can mitigate the neutralization effectiveness of the base by the acid which exists in an environment which carried out optical generating. For this reason, a good relief pattern is formed.

(3) The base reactivity resin containing a base growth agent can raise the cure rate and hardening property of resin which are represented by the epoxy resin.

(4) The base growth agent of this invention can make the reaction of the base active substance start by heating or optical exposure by adding this to the base active substance combining a base generating agent.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the base growth agent and base growth agent constituent which generate a base according to an operation of a base, a base reactivity constituent, a photosensitive constituent, and the pattern formation approach.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] It is put in practical use in many fields that the chemical structural change produced according to an operation of actinic rays, such as light, infrared radiation, far infrared rays, an electron ray, or an X-ray, is used for the resin sensed for actinic rays or its constituent as an image formation ingredient, or it uses hardening of a monomer or a prepolymer for surface coating processing etc. Although it is the light which is widely used among actinic rays and actinic rays are hereafter specified and explained to light, the actinic rays to the resin of this invention or its constituent are not limited to light. The sensitization rate in these resin or its constituent, a sensitization wavelength field, and definition are various, these suitable properties are chosen according to the purpose, and the photopolymer or constituent suitable for it is chosen. However, the essential trouble as follows existed, respectively. Although the photopolymer which uses polymeric materials as a principal component reaches far and wide as a photosensitive ingredient in which it is mass-produced and high definition is shown and it came to be used (refer to Yamaoka, edited by Nagamatsu, "photopolymer technology", and Nikkan Kogyo Shimbun (1988)), in order to shorten the time amount required for forming an image and a pattern, maintaining the outstanding definition, development of the further photosensitive high sensitivity ingredient is desired.

[0003] In order to raise the sensitization rate of the photopolymer ingredient for image formation, various attempts have so far been made. But it is the photopolymerization system to which having been widely set as the object of development carries out the polymerization of many vinyl monomers continuously by making into an initiator the radical kind generated in an operation of light. Moreover, the cationic polymerization system which is made to generate an acid in an operation of light and makes this acid a catalyst is also the object of active development. Since these polymerization reactions carry out induction of the chemical change of the low-molecular matter which carried out dissolution distribution into the high polymer itself or a macromolecule, they can use for image formation physical-properties change produced as a result. However, in the case of a radical polymerization, since a polymerization reaction is checked by the oxygen in air, by the thin film system, the special device for oxygen cutoff is needed especially. The configuration of the relief pattern form since it be neutralize by the minute amount alkali to which the strong acid generate from a photo-oxide generating agent exist in an environment by optical exposure, although it be advantageous be spoil at the point which, on the other hand, do not have such oxygen inhibition effectiveness by the optical cationic polymerization system, and the problem that definition fall in cost price be point out in the field of the micro or the resist ingredient for nano lithography.

[0004] On the other hand, practical use is widely presented with the technique of stiffening resin according to an operation of light and a quantum line for a short time, as what realizes high-speed processing of a surface coating object and a non-solvent surface treatment process. Although the radical polymerization is broadly utilized also for this purpose, the inhibition effectiveness by the oxygen in air must be taken into consideration. With the hardening technique of using cationic polymerization, although it was advantageous since there was no inhibition effectiveness of oxygen, problems by the strong acid as an initiator, such as corrosion and the denaturation of resin, remained. Moreover, practical use is similarly presented with the

hybrid mold-curing technique which combined the exposure and heat treatment by light or the electron ray widely as what realizes high-speed processing of a surface coating object and a non-solvent manufacture process. Furthermore, although the sensible-heat hardening resin constituent of 1 acidity or alkalinity which took in the principle which generates an acid and a base thermally potentially was also widely set as the object of examination, it looked forward to all performing hardening in a heat treatment process more quickly from a viewpoint of energy saving.

[0005] Using the polymerization reaction and chemical reaction by the base catalyst as one method of conquering such a trouble is proposed. For example, there is the approach of making generate the amine as a base and carrying out chemistry denaturation of the resin by making this into a catalyst according to an operation of light and heat. It is applicable to image formation using a soluble change before and after chemistry denaturation. However, the generating effectiveness of the base generated in an operation of light has come to have sufficient sensibility practical from a low thing etc. On the other hand, since the resin which has an epoxy group causes crosslinking reaction by operation of a base and it stiffens an epoxy resin, it generates the amines as an initiator or a catalyst within an epoxy system resin layer according to an operation of light and heat, and, subsequently there is [the approach of stiffening by heat-treatment etc.]. However, in this case, since the engine performance of the ingredient which can be hardened according to an operation of light and an electron ray is low, practical use has come to be presented with it.

[0006] Thus, in order to high-performance-ize further the **** formation and the hardening technique based on a radical kind, a cation kind, the polymerization reaction further started with a base kind, or a chemical reaction, the inhibition effectiveness by the oxygen in air is not received, but excluding a staining substance like the strong acid to generate, it is still more efficient and a resin constituent with which a reaction advances is desired strongly.

[0007] In catalytic reaction, in order that the number of the catalyst molecules which involve there may not change, according to a certain poisoning operation, a catalyst deactivates and a reaction stops it. Or catalytic reaction stops also by controlling diffusion in a solid-state strongly. Therefore, what is necessary is just to make the number of the molecules which have a catalysis increase in process of catalytic reaction, in order to make catalytic reaction make it efficient further. Namely, what is necessary is to decompose in autocatalysis and just to find out the matter which generates the molecule which newly has catalyst ability. It decomposes in [actually until now] autocatalysis, strong acid is generated, and the acid growth reaction which has the property that the concentration of strong acid increases nonlinearly is proposed (Arimitsu, Ichimura, the high sensitivity organic system light image formation ingredient incorporating a growth reaction, a functional material, 17 (12), 16 -24 (1997) reference). Thus, the acid growth agent which an acid increases in growth is found out, and the resin constituent with which high performance-ization is attained is also known by adding them (KArimitsu, KKudo and KIchimura, J.Am.Chem.Soc., 120, 37 -45 (1998) reference).

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] (1) Since the sensibility of the photosensitive constituent containing the base growth agent of this invention improves sharply, it can be used for a high sensitivity image formation ingredient.

(2) Since the yield of a base increases sharply by the base growth agent, it can mitigate the neutralization effectiveness of the base by the acid which exists in an environment which carried out optical generating. For this reason, a good relief pattern is formed.

(3) The base reactivity resin containing a base growth agent can raise the cure rate and hardening property of resin which are represented by the epoxy resin.

(4) The base growth agent of this invention can make the reaction of the base active substance start by heating or optical exposure by adding this to the base active substance combining a base generating agent.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention makes it the technical problem to offer the pattern formation approach using the photosensitive constituent while offering the base growth agent which decomposes itself and generates a new base according to an operation of a base, a base growth agent constituent, a base reactivity constituent, and a photosensitive constituent.

[Translation done.]

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MEANS

[Means for Solving the Problem] this invention person came to complete this invention, as a result of repeating research wholeheartedly that said technical problem should be solved. That is, according to this invention, it consists of an urethane system compound containing at least one urethane bond, and the base growth agent characterized by for an operation of the base of the amino-group origin which forms this urethane bond decomposing, and this urethane system compound generating the base of this urethane bond origin is offered. Moreover, according to this invention, the base growth agent constituent characterized by consisting of said base growth agent and a base generating agent is offered. Furthermore, according to this invention, the base reactivity constituent characterized by consisting of said base growth agent, a base generating agent, and the base active substance is offered. According to this invention, the photosensitive constituent characterized by consisting of a base growth agent, an optical base generating agent, and a polymerization nature epoxy compound is offered further again. According to this invention, the pattern formation approach characterized by using said photosensitive constituent as a pattern formation ingredient is offered further again.

[0010]

[Embodiment of the Invention] When the base growth agent of this invention makes the same base as the base which decomposes according to an operation of a base, and generates a base, and is generated in this case act, it has the property of decomposing and generating a base. Therefore, the base of the equivalent smaller than it is made to only act to the constant rate, it decomposes in self-multiplication, finally the whole quantity decomposes, and the base growth agent of this invention generates a lot of bases corresponding to the base growth dose.

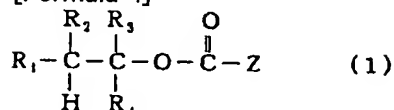
[0011] The base growth agent of this invention consists of an urethane system compound which has said property. That is, the base growth agent of this invention consists of an urethane system compound containing at least one urethane bond, an operation of the base (ammonia or amine) of the amino-group origin which forms this urethane bond decomposes this urethane system compound, and it is characterized by generating the base (ammonia or amine) of this urethane bond origin. Of course, even if it makes a different base from the base of the amino-group origin which forms the urethane bond act, it decomposes and a base is generated.

[0012] Until now, although various kinds of urethane system compounds are known, there is nothing that has been recognized as a base growth agent. It can be judged by the easy preliminary experiment shown below whether the urethane system compound has a function as a base growth agent.

(Base growth diagnosis) the base HNR one R2 same to the amino group NR one R2 which forms the urethane bond (-OCONR one R2) of the urethane system compound in the 2wt% methanol-d4 solution of an urethane system compound as the base of the origin — 0.1wt(s)% — after putting the added solution into NMR spectrum test sample tubing and carrying out the sealed tube of this, it heats at 100 degrees C and an NMR spectrum is measured. By the increment in the NMR signal of the olefin generated by disassembly of an urethane compound, an urethane system compound is judged to be what has a base growth function.

[0013] Generally the base growth agent of this invention consists of an urethane system compound expressed with the following general formula (1).

[Formula 4]

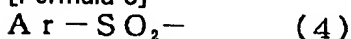


R1 and R2 are hydrogen, a substituent, or an electronic suction nature machine among said formula, and at least one of these is an electronic suction nature machine. R3 and R4 are hydrogen or a substituent, and Z is an amino group.

[0014] In organic electron theory etc., the electronic suction nature machine of common use, for example, a fluorenyl group, an organic sulfoxide radical, a cyano group, a nitro group, an ester group, a carbonyl group, an amide group, a pyridyl radical, etc. are included by said electronic suction nature machine.

[0015] What is expressed with the following general formula (4) is included by said organic sulfoxide radical.

[Formula 5]

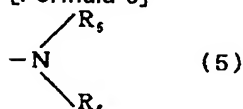


the inside of said formula, and Ar -- an organic radical -- it is an aryl group preferably. Phenyl, tolyl, naphthyl, etc. are mentioned as the example. the carbon number of Ar -- 6-18 -- it is 6-12 preferably.

[0016] said substituent -- carbon numbers 1-12 -- desirable -- the alkyl group of 1-6, and carbon numbers 5-10 -- desirable -- the cycloalkyl radical of 6-8, and carbon numbers 6-14 -- desirable -- the aryl group of 6-10, and carbon numbers 7-15 -- the arylated alkyl radical of 7-11 etc. is included preferably. As the example, methyl, ethyl, propyl, butyl, cyclohexyl, phenyl, tolyl, naphthyl, benzyl, phenethyl, naphthyl methyl, etc. are mentioned.

[0017] The non-permuted amino group and the permutation amino group are included by said amino group. The mono-permutation amino group and the II permutation amino group are included by the permutation amino group. Said amino group can be expressed with the following general formula (5).

[Formula 6]

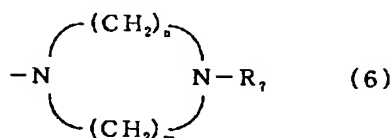


[0018] R5 and R6 show hydrogen or an organic radical among said formula. the carbon number of an organic radical -- 1-18 -- it is 6-12 preferably. An alkyl group, a cycloalkyl radical, an aryl group, and an arylated alkyl radical are included by this organic radical. as an alkyl group -- especially -- carbon numbers 1-12 -- the thing of 2-6, for example, ethyl, propyl, butyl, hexyl, etc. are mentioned preferably. as a cycloalkyl radical -- carbon numbers 5-10 -- the thing of 6-8, for example, cyclohexyl, cyclo octyl, etc. are mentioned preferably. as an aryl group -- carbon numbers 6-14 -- the thing of 6-10, for example, phenyl, tolyl, naphthyl, etc. are mentioned preferably. as an arylated alkyl radical -- a carbon number -- 7-15 -- the thing of 7-11, for example, benzyl, phenethyl, naphthyl methyl, etc. are mentioned preferably. Said alkyl group, the cycloalkyl radical, the aryl group, and the arylated alkyl radical may have the substituent. As a substituent in this case, the amino group, an alkoxy group, an alkoxy carbonyl group, an acyl group, an acyloxy radical, a hydroxy group, etc. are mentioned.

[0019] In the amino group of said general formula (5), R5 and R6 can be connected and they can form a nitrogen ring. the number of annular atoms of the nitrogen ring in this case -- 3-12 -- it is 5-8 preferably. Moreover, said nitrogen ring can contain two or more hetero atoms (N, O, S, etc.) in the annular atoms.

[0020] In this invention, what is expressed with the following general formula (6) can be mentioned as a desirable thing as said amino group.

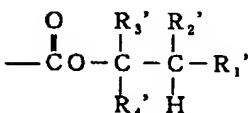
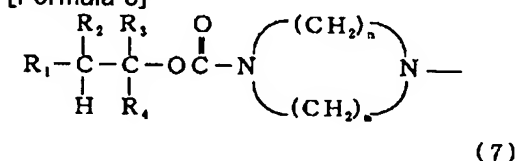
[Formula 7]



[0021] the inside of said formula, and n and m -- 1-6 -- the number of 2-4 is shown preferably. n+m -- 4-12 -- it is 4-8 preferably. Although R₇ shows substituents, such as a hydrocarbon group besides hydrogen, a hydrocarbon oxy-radical, and an acyl group, it may be residue of an urethane system compound which has a base growth function. the carbon number of the hydrocarbon group in the hydrocarbon group in a hydrocarbon group and a hydrocarbon oxy-radical, and an acyl group -- 1-12 -- it is 1-8 preferably. Alkyl, cycloalkyl, aryl, and arylated alkyl are included by this hydrocarbon group.

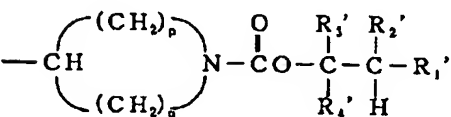
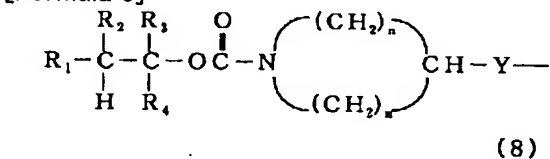
[0022] The urethane system compound used as a base growth agent of this invention can contain two or the urethane bond beyond it. As such an urethane system compound, what is expressed with the following general formula (7) and (8) can be mentioned.

[Formula 8]



[0023]

[Formula 9]



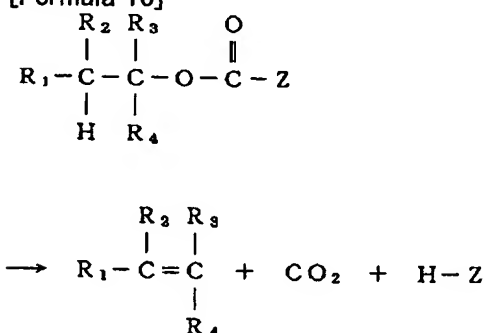
[0024] In said general formula (7), R₁ and R₂ are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R₃ and R₄ are hydrogen or a substituent. R₁' and R₂' are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R₃' and R₄' are hydrogen or a substituent. n and m -- 1-6 -- the number of 2-4 is shown preferably. n+m -- 4-12 -- it is 4-8 preferably.

[0025] In said general formula (8), R₁ and R₂ are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R₃ and R₄ are hydrogen or a substituent. R₁' and R₂' are hydrogen, a substituent, or an electronic suction nature machine, and at least one of these is an electronic suction nature machine. R₃' and R₄' are hydrogen or a substituent. Y -- carbon numbers 1-8 -- it is the alkylene group of 2-6 preferably. n and m -- 1-6 -- the number of 2-4 is shown preferably. n+m -- 4-12 -- it is 4-8 preferably. p and q -- 1-6 -- the number of 2-4 is shown preferably. p+q -- 4-12 -- it is 4-8 preferably.

[0026] As an example of said electronic suction nature machine and a substituent, what was shown in connection with said general formula (1) can be illustrated.

[0027] The base growth agent of this invention is characterized by the electronic suction nature machine and the hydrogen atom having combined with the carbon atom contiguous to the carbon atom which contains a urethane bond and the urethane group (carbamoyle group) combines on the molecular structure. Therefore, the hydrogen atom combined with the carbon atom which the electronic suction nature machine has combined for such a structural description is tintured with an acid-property, and drawing is possible for it by operation of a base. If the mechanism of the base growth reaction by the base growth agent of this invention is shown, first, drawing of said hydrogen atom will happen according to an operation of a base, subsequently carbamic acid will ****, this will decompose further, and a base and a carbon dioxide will be generated. And the base generated on this occasion acts on other base growth agent molecules, that molecule is made to disassemble, and a base is generated. Thus, it is decomposed in chain reaction and a base growth agent can generate a lot of bases by a small amount of base after all. It is as follows when a reaction formula shows said base growth reaction taking the case of the urethane system compound of said general formula (1).

[Formula 10]

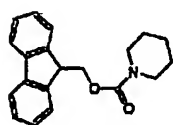


The base of the amino-group origin which H-Z in said reaction formula has combined with the urethane bond is shown. this base — ammonia — or it is an amine preferably. What is necessary is to make chloro formate react to alcohol, to generate asymmetric carbonic acid diester and just to make a base react subsequently to this carbonic acid diester, in order to prepare the base growth agent of this invention.

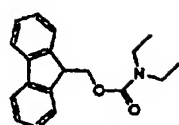
[0028] The example of the base growth agent of this invention is shown below.

[0029]

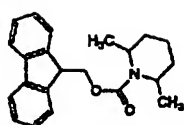
[Formula 11]



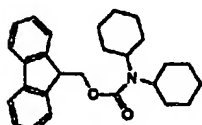
1-1



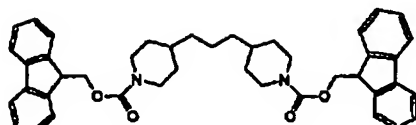
1-2



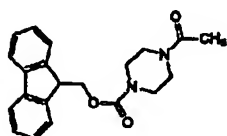
1-3



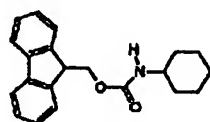
1-4



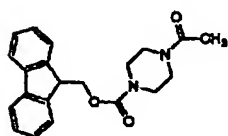
1-5



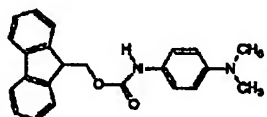
1-6



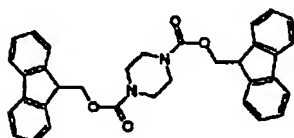
1-7



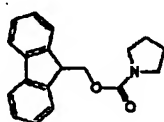
1-8



1-9



1-10



1-11

[0030]

[Formula 12]

CC(C)OC(=O)N1CCCCC1CS(=O)(=O)c2ccccc2

2-1

CC(C)(OCC(=O)N1CCCCC1CCCCC1N2CCCCC2C(=O)OCC3C(C)C(C)C3)CC(=O)N4CCCCC4C(=O)OCC5C(C)C(C)C5S(=O)(=O)c6ccccc6

2-2

CC(C)(OCC(=O)N1CCN(CC1)C(=O)OCC(C)CSC2=CC=CC=C2)CCSC3=CC=CC=C3

2-3

CS(=O)(=O)CC(C)(C)OC(=O)N1CCCC1

2-4

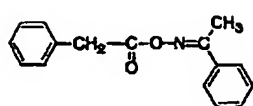
[0031] Said compound of No.1-1-1-11 shows the example of the fluorene system base growth agent which the fluorenyl group has combined as an electronic suction nature machine, and generates an amine in growth. On the other hand, said compound of No.2-1-2-4 shows the example of the sulfone system base growth agent which the organic sulfoxide radical has combined as an electronic suction nature machine, and generates an amine in growth.

[0032] The base growth agent of this invention is thermally stable at a room temperature, and can be saved over a long period of time. If little addition of the base which dissolves this base growth agent into an organic solvent, and triggers early catalytic reaction in this is carried out and it carries out a pyrogenetic reaction — from specific reaction time — rapid — decomposition — happening — SIG — the reaction curve which consists of a MOIDARU curve is given, and it can check that the base growth reaction is advancing from now on.

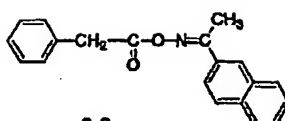
[0033] The base growth agent constituent of this invention is a constituent containing a base growth agent and a base generating agent. This constituent can have the shape of liquefied or a solid-state. What generates a base with heating, the thing which generates a base by the exposure of activity energy lines (electromagnetic waves, electron rays, etc., such as light and an X-ray) are included by the base generating agent. Conventionally, such a base generating agent is well-known, and can use various kinds of things. For example, as a base generating agent which generates a base according to an operation of light, what is used for a chemistry magnification mold photoresist is used ("imaging business the volume on owner ** electronics ingredient research community, organic material", the **** exudation version (refer to 1993)). Moreover, in order to expand the sensitization wavelength field of these optical base generating agents, a photosensitizer can also be made to live together suitably. With the photoreaction nature matter, the base generated by the photolysis of these matter acts on a base growth agent, and promotes generating of a base. The optical base generating agent preferably used for this invention below is illustrated.

[0034]

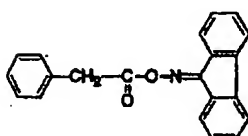
[Formula 13]



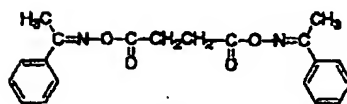
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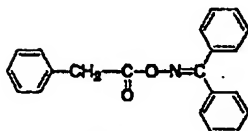
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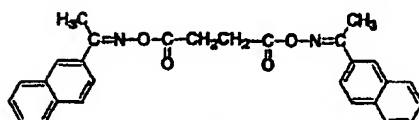
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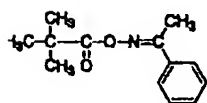
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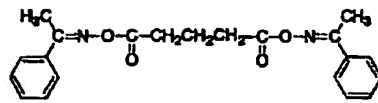
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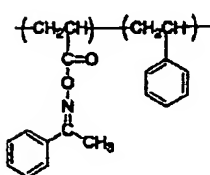
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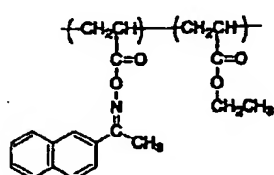
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3-8



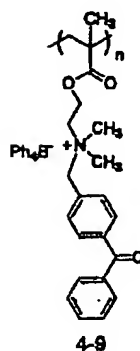
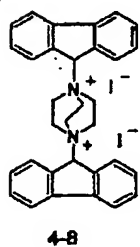
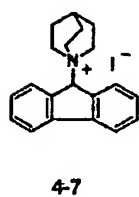
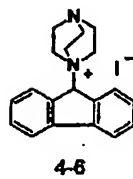
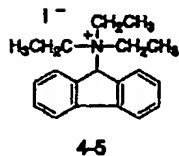
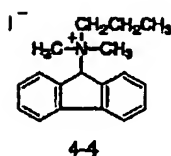
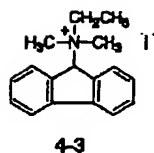
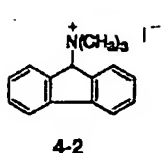
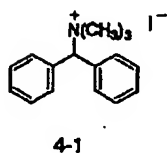
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3-10

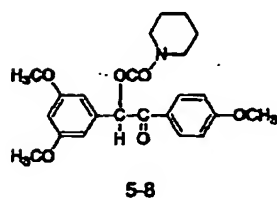
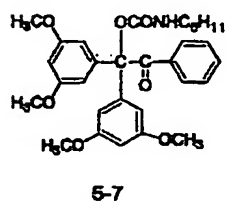
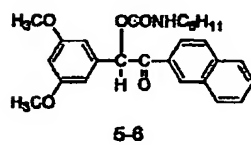
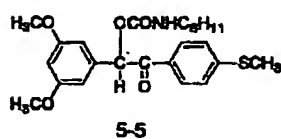
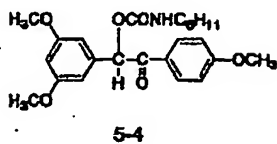
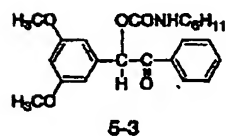
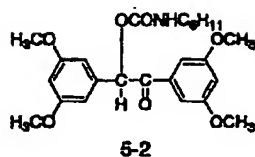
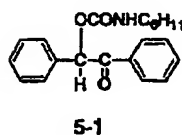
[0035]

[Formula 14]



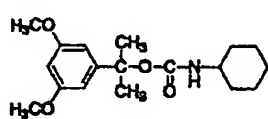
[0036]

[Formula 15]

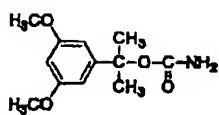


[0037]

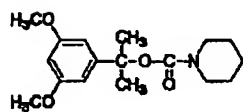
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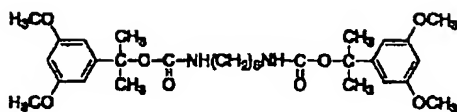
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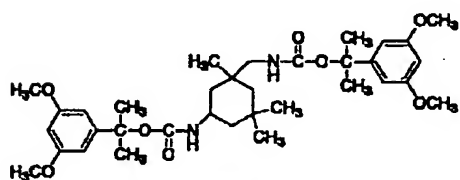
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6-3



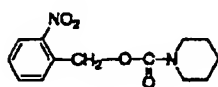
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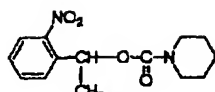
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[0038]

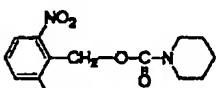
[Formula 17]



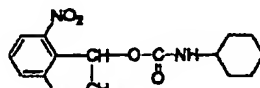
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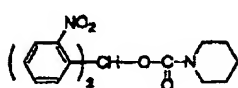
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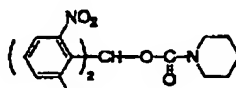
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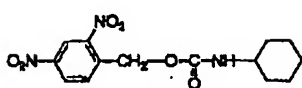
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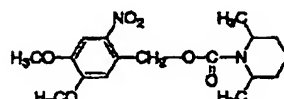
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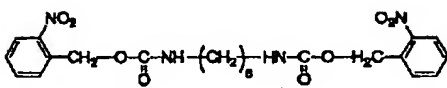
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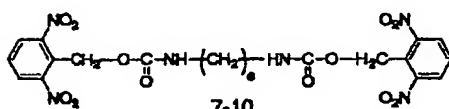
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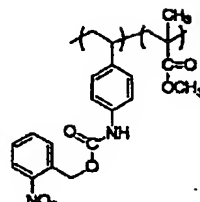
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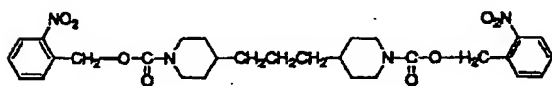
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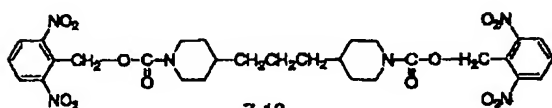
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7-11



7-12



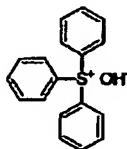
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[0039]

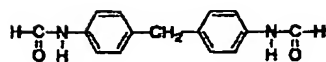
[Formula 18]



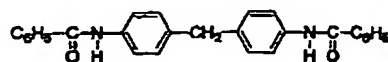
8-1



8-2



8-3



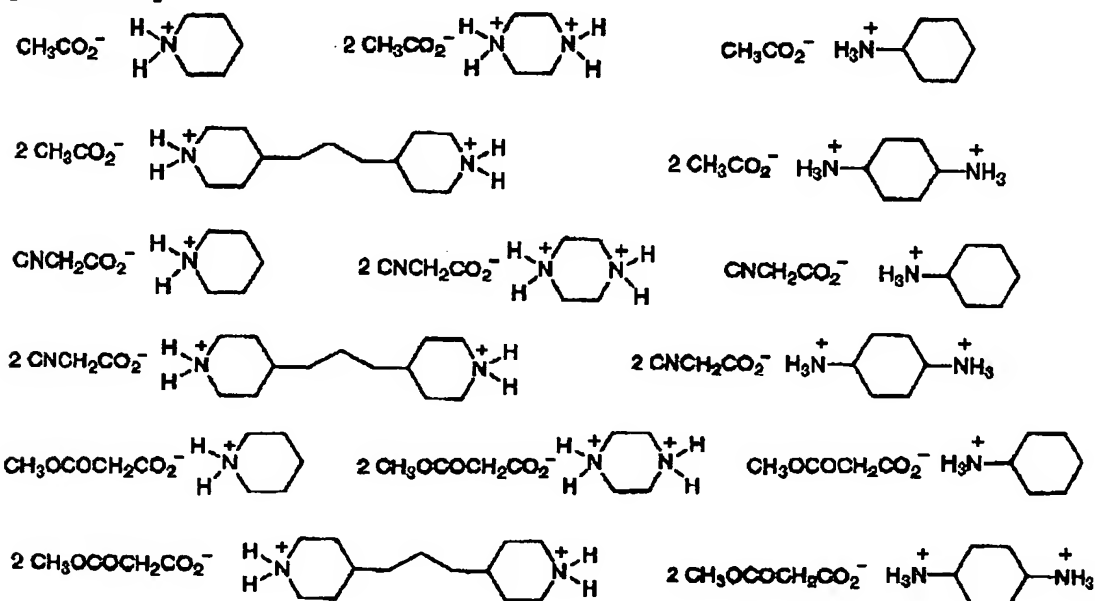
8-4

[0040] Said compound of No.3-1-No.3-10 is an oxime ester system compound, generates a

Schiff base according to an operation of light, and generates an amine by this hydrolysis. Here, the compound of No.3-9 and No.3-10 is a high molecular compound, and generates an amine by the optical exposure to the macromolecule side chain. The compound of No.4-1-No.4-9 is an ammonium system compound, and generates the third class amine by the photolysis. The compound of No.5-1-No.5-8 is a benzoin system compound, and generates an amine by the photolysis. The compound of No.6-1-No.6-5 is a dimethoxy benzyl urethane system compound, and generates an amine by the photolysis. The compound of No.7-1-No.7-13 is an alt.nitrobenzyl urethane system compound, and generates an amine by the photolysis. Other optical base generating agents are shown in No.8-1-No.8-4. The compound of No.8-1 generates ammonia as a base by the exposure of light. The compound of No.8-2 generates hydroxide ion as a base by the exposure of light. The compound of No.8-3 generates an amine as a base by the exposure of light. The compound of No.8-4 generates an amine as a base by the exposure of light. As a compound which generates a base with heating, the following can be shown, for example.

[0041]

[Formula 19]

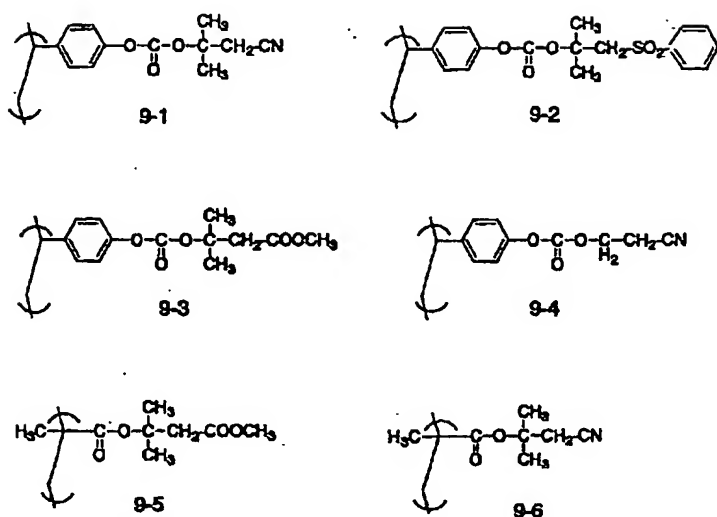


[0042] In the base growth agent constituent containing the base growth agent and base generating agent by this invention, although especially the rate of the base generating agent is not restrained, it is a weight ratio to a base growth agent, and is usually 5 - 40 % of the weight preferably one to 100% of the weight. Said base growth agent constituent generates the base in growth according to an operation of heat, light, etc. This constituent can make the reaction of that base active substance start by heating or optical exposure by blending this with various kinds of base active substance.

[0043] The base reactivity constituent of this invention is a constituent containing the base active substance, a base growth agent, and a base generating agent. This constituent can have the shape of liquefied or a solid-state. One sort or two sorts or more of chemicals which occur chemical reactions, such as a decomposition reaction, and an elimination reaction, a condensation reaction, a polymerization reaction, are included according to an operation of a base by the base active substance. This chemical can be the low-molecular matter, oligomer, a high polymer (polymer), etc. The base active substance can be a high polymer permuted by the residue which causes a base catalyst reaction, and can be the resin constituent or polymer which shows a condensation reaction by the base catalyst. Those examples are shown below.

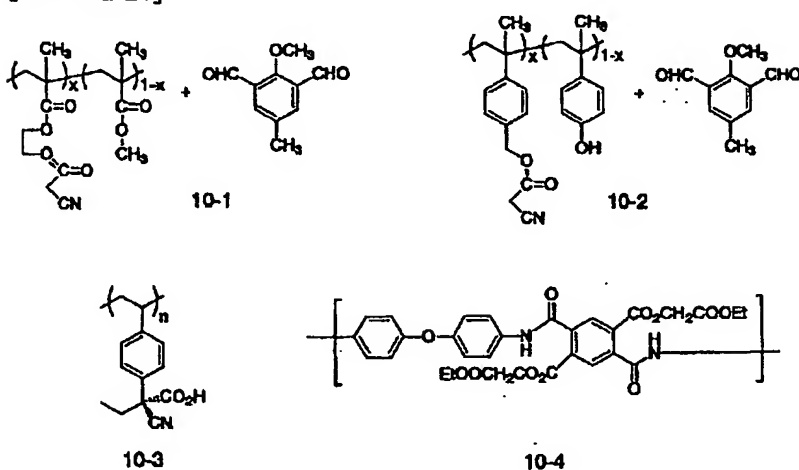
[0044]

[Formula 20]



[0045]

[Formula 21]

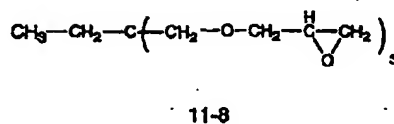
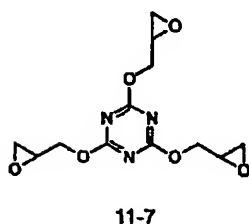
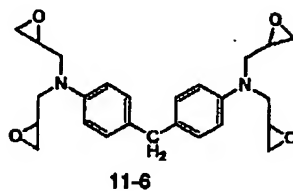
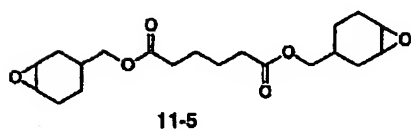
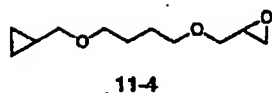
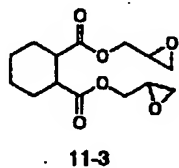
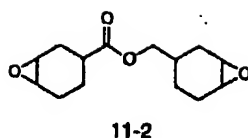
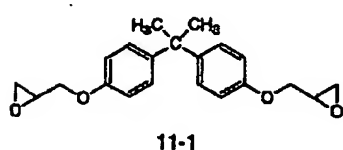


[0046] The compound of No.9-1-No.9-4 produces the reaction of desorption and a decarboxylation according to an operation of a base among said high molecular compounds of No.9-1-No.9-6. The compound of No.9-5 and No.9-6 produces the reaction of a decarboxylation according to an operation of a base. The matter (mixture) of No.10-1 produces the reaction of dehydration condensation and bridge formation according to an operation of a base among said base active substance of No.10-1-No.10-4. The matter (mixture) of No.10-2 produces the reaction of dehydration condensation and bridge formation according to an operation of a base. The matter (polymer) of No.10-3 produces the reaction of a decarboxylation according to an operation of a base. The matter of No.10-4 produces the reaction of imide formation according to an operation of a base.

[0047] The base active substance can be matter which has at least one epoxy group. By making a base (amine) act on the compound which has at least two epoxy groups, the epoxy compound can be made into a polymer by the ring opening polymerization of the epoxy group. Moreover, chemistry denaturation of the epoxy compound can be carried out by carrying out the addition reaction of the amine to an epoxy compound. The example of an epoxy compound which shows polymerization reactivity is shown below.

[0048]

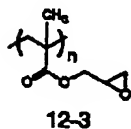
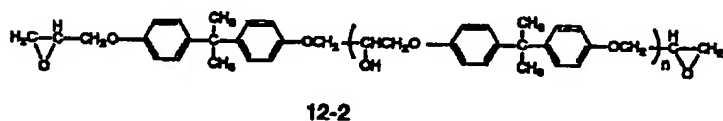
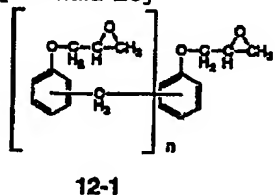
[Formula 22]



[0049] The example of other epoxy compounds (epoxy resin) in which polymerization reactivity is shown is shown below.

[0050]

[Formula 23]



[0051] In said base reactivity constituent, the rate of a base growth agent is usually about 2 - 30 % of the weight preferably one to 60% of the weight to the base active substance. When there are too few loadings of a base growth agent, it becomes impossible to make the base active substance react quickly. On the other hand, if many [too], the amount of the base generating agent used will increase, and the base generating agent itself will have big effect on the solubility of the base active substance, and it is disadvantageous in price. A base generating agent is good

to specify to 2 - 15% of the weight of within the limits especially preferably one to 20% of the weight to the base active substance.

[0052] The desirable base reactivity constituent by this invention is a polymerization reactivity constituent containing a polymerization nature epoxy compound. According to an operation of light or heat, the polymerization of such a constituent is carried out and it gives a polymer.

[0053] The desirable base reactivity constituent by this invention is a constituent which starts a polymerization reaction by light. This constituent is a constituent which consists of a polymerization nature epoxy compound, a base growth agent, and an optical base generating agent, and contains auxiliary components, such as a curing agent for polymerization nature epoxy compounds, and a hardening accelerator, other bulking agents, if needed. This constituent is advantageously used as a pattern formation ingredient. In order to form a pattern using this photosensitive constituent, this photosensitive constituent is dissolved in an organic solvent, coating liquid is made, this coating liquid is applied to the solid-state front face where a substrate etc. is suitable, it dries and a paint film is formed. To this paint film, pattern exposure is performed and a base is generated. Subsequently, it heat-treats and a chain of decomposition of a base growth agent is urged. although the conditions of heat-treatment are changed according to the class of base growth agent [activity / base / exposure energy and / to be used], the class of epoxy compound, etc. — whenever [stoving temperature] — the range of 60 to 150 degrees — it is the range of 80 to 130 degrees more preferably. Heating time is 5 minutes from 30 seconds more preferably from 10 seconds for 10 minutes. Negatives are developed by immersing this into the solvent which produces a difference in solubility in the exposure section and the unexposed section, and a pattern is obtained.

[Translation done.]

* NOTICES *

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] Next, this invention is explained in full detail according to an example.

[0055] Example 19-fluorenyl methyl chloroformate 2.00g was dissolved in ether 50ml, and the ether solution of one to 31 g HIPERIJIN was dropped at this under ice-cooling. After stirring at a room temperature for 20 minutes under ice-cooling for 1.5 hours, the reaction solution was washed in order of water, 5% hydrochloric acid, and saturation brine, and the organic layer was dried with sulfuric anhydride magnesium. The solid-state obtained by carrying out solvent distilling off was recrystallized in ethanol, and 0.98g N-(9-fluorenyl methoxy carbonyl) piperidine (No.1-1) was obtained as a white crystal.

[0056] 47% melting point of 98-101 degrees C 1 H-NMR (90MHzCDCl₃) delta (ppm):1.55 (brs, 6H, CH₂) of yield, 3.3-3.6 (m, 4H, CH₂), 4.1-4.5 (m, 3H, CH, CH₂), 7.1-7.7 (m, 8H, Ar-H)
IR(KBr)(cm⁻¹):2936,1686,1437,1259,1232,1151,1106,762,739.

Calculated value as C₂₀H₂₁NO₂: C, 78.14;H, 6.89;N, 4.56%. Analysis value: C, 77.90;H, 6.72;N, 4.41%.

[0057] Like example 2 example 1, 9-fluorenyl methyl chloroformate was made to react with diethylamine, the column chromatography (bulking agent; silica gel (WAKOGERU C-200), expansion solvent; hexane:ethyl-acetate =20:1) refined the obtained product, and the 1.97g 9-fluorenyl methyl N-diethyl carbamate (No.1-2) was obtained as a colorless liquid.

[0058] 86.4% 1 H-NMR (90MHz, CDCl₃) delta (ppm):1.04 (t,H₂ [J= 7.2], 4H, CH₂) of yield, 4.1-4.5 (m, 3H, CH, CH₂), 7.1-7.9 (m, 8H, Ar-H)

IR(neat)(cm⁻¹):2974,1696,1478,1451,1426,1273,1168,757,739.

Calculated value as C₁₉H₂₁O₂N: C, 77.25;H, 7.17;N, 4.74%. Analysis value: C, 76.92;H, 7.18;N, 4.80%.

[0059] By the same actuation as example 3 example 1, 9-fluorenyl methyl chloroformate was made to react with cis-2 and 6-dimethyl piperidine, the column chromatography (bulking agent; silica gel (WAKOGERU C-200), expansion solvent; hexane:ethyl-acetate =20:1) refined the obtained product, and 2.25g N-(9-fluorenyl methoxy carbonyl)-cis-2 and 6-dimethyl piperidine (No.1-3) was obtained as a white crystal.

[0060] 86.9% melting point 80of yield -82degree-C1H-NMR(90MHz, CDCl₃) delta(ppm): — 1.10 (s, 3H, CH₃), 1.19 (s, 3H, CH₃), 1.3-1.9 (m, 6H, CH₂), and 7.1-7.9 (m, 8H, Ar-H)

IR(KBr)(cm⁻¹):2944,1703,1447,1409,1307,1085,763,738.

Calculated value as C₂₂H₂₅NO₂: C, 78.77;H, 7.51;N, 4.18%. Analysis value: C, 78.84;H, 7.57;N, 4.14%.

[0061] By the same actuation as example 4 example 1, 9-fluorenyl methyl chloroformate was made to react with dicyclohexylamine, the obtained solid-state was recrystallized in ethanol, and the 9-fluorenyl methyl N-dicyclohexyl KARUPA mate (No.1-4) was obtained as a white crystal.

[0062] 71.5% melting point of 190-194 degrees C 1 H-NMR (90MHz, CDCl₃) delta (ppm):0.5-2.0 (m, 22H, CH₂) of yield, 4.20 (t, J= 4.6Hz, 1H, CH) and 4.62 (d, J= 4.6Hz, 2H, CH₂O), 7.1-7.9 (m, 8H, Ar-H)

IR(KBr)(cm⁻¹):2926,1674,1441,1290,1238,1167,1119,1046,744.

Calculated value as C₂₇H₃₃NO₂: C, 80.37;H, 8.24;N, 3.47%. Analysis value: C, 80.56;H, 8.32;N, 3.42%.

[0063] 9-fluorenyl methyl chloroformate is made to react with a 1 and 3-G 4-piperidyl propane by the same actuation as example 5 example 1. the oil of the shape of an acquired starch syrup — a column chromatography (bulking agent; — silica gel (WAKOGERU C-200) —) expansion solvent; — hexane: — it refined by ethyl-acetate =2:1 and 9.10g 4 and 4'-[screw [[(9-fluorenyl methyl) oxy-] carbonyl] trimethylene] dipiperidine (No.1-5) was obtained as a white crystal.

[0064] 36.0% melting point of 109 degrees C 1 H-NMR (90MHz, CDCl₃) delta (ppm):0.8-1.9 (m, 16H, CH, CH₂) of yield, 2.5-30 (br, 4H, N-CH₂), 3.9-4.5 (m, 10H, CH, CH₂O, N-CH₂), 7.1-7.9 (m, 16H, Ar-H)

IR(KBr)(cm⁻¹):2918,1695,1432,1217,1146,1103,759,741.

Calculated value as C₄₃H₄₆N₂O₄: C, 78.86;H, 7.08;N, 4.28%. Analysis value: C, 78.93;H, 7.21;N, 4.20%.

[0065] It is 1 and 1 in 10ml of example 6 N,N-dimethylacetamide. — It added to the solution which added dimethyl-2-(phenyl sulfonyl) ethyl p-nitrophenyl carbo NATO 1.50g (3.95mmol) and 1-hydroxy benzotriazol 0.162g (0.120mmol), stirring the piperidine 1.36g (16.0mmol) solution which dissolved in 10ml of N,N-dimethylacetamide at a room temperature. The reaction solution was stirred at 50 degrees C with the room temperature for 3 hours for 6 hours. This reaction solution was poured out into 400ml of 1% sodium-hydrogencarbonate water solutions, the generated precipitate was filtered, and it washed with water. Precipitate was dissolved in the ether, reduced pressure distilling off of the solvent was carried out after desiccation with sulfuric anhydride magnesium, and 0.91g N-[1 and 1-dimethyl-2-(phenyl sulfonyl) ethoxycarbonyl] piperidine (No.2-1) was obtained as a white crystal.

[0066] 70.0% melting point [of yield]: — 104-105-degree-C 1 H-NMR(90MHz, CDCl₃) delta (ppm):1.43- 1.55 (br, 6H, N-CH₂, CH₂), 1.67 (s, 6H, CH₃), and 3.1-3.3(m,4H,N-CH₂),3.89(s,2H,CH₂),7.3-8.0(m,5H,Ar-H).

IR(KBr)(cm⁻¹):1689(C=O),1310(SO₂),1143(SO₂)

Calculated value as C₁₆H₂₃O₄NS: C, 59.05;H, 7.12;N, 4.31;S, 9.85%. Analysis value: C, 59.07;H, 6.95;N, 4.30;S, 9.89%.

[0067] By the same actuation as example 7 example 6, it is 1 and 1-dimethyl -2 (phenyl sulfonyl) ethyl p. -Phenyl carbo NATO and a 1 and 3-G 4-piperidyl propane were made to react 2 fatty tuna, and the column chromatography (bulking agent; silica gel (WAKOGERU C-200), expansion solvent; hexane:ethyl-acetate =2:1) refined the obtained solid-state. The product was dissolved in chloroform, it refined by the reprecipitating method using a hexane, and 1.93g 4 and 4'-[screw [[1[1 and]-dimethyl-2-(phenyl sulfonyl) ethyl oxy-] Carbonyl] trimethylene] dipiperidine (No.2-2) was obtained as a white crystal.

[0068] yield: — 53.0% melting point: — 139-140-degree-C 1 H-NMR (90MHz, CDCl₃) delta (ppm):1.14-1.80 (m, 28H, CH₃, CH₂, CH), 2.40-2.69 (br, 4H, N-CH₂), 3.76-4.04 (m, 8H, N-CH₂, SO₂CH₂), and 7.4-8.0 (m, 10H, Ar-H)

IR(KBr)(cm⁻¹):1688(C=O),1318(SO₂),1214(SO₂)

Calculated value as C₃₅H₅₀O₈N₂S₂: C, 60.84;H, 7.29;N, 4.06;S, 9.28%. Analysis value: C, 60.56;H, 7.05;N, 4.06;S, 8.75%.

[0069] Example 8 Pori (glycidyl methacrylate) and the cyclohexanone solution which contains 4 and 4'-[screw [[(2-nitrobenzyl) oxy-] Carbonyl] trimethylene] dipiperidine (7-12) which is a 10wt (s)% optical base generating agent to this polymer were prepared. this solution — the base growth agent 4 and 4'-[screw [[(9-fluorenyl methyl) oxy-] carbonyl] trimethylene] dipiperidine (No.1-5) — a polymer — receiving — 43wt(s)% — it added and considered as the solution of a photosensitive constituent. Spin spreading of this solution was carried out on silicon UNIH on 1000rpm and the conditions for 30 seconds, and it prebaked by heating for 1 minute at 100 degrees C. After carrying out UV irradiation to this paint film, it heated for 15 minutes at 100 degrees C, and postbake processing was performed. Furthermore, it was immersed in 2-methoxy ethyl acetate for 30 seconds, and this film was developed. It washed and dried by ethanol, thickness was measured, and the sensitivity curve was searched for. Consequently, it turned out by adding a base growth agent that sensibility of single figure improves rather than the system under base growth agent un-existing. Moreover, after carrying out UV irradiation of the film which carried out spin spreading over the photo mask, the clear negative-mold image was

obtained by washing of 2-methoxy ethyl acetate.

[0070] 2-methoxy ethyl acetate solution containing 4 and 4'-[screw-[[[(2-nitrobenzyl) oxy-] Carbonyl] trimethylene] dipiperidine (7-12) which is example 9 Pori (glycidyl methacrylate) and a 10wt% optical base generating agent was prepared. this solution — the base growth agent 4 and 4'-[screw [[[(1 and 1-dimethyl -2 (phenyl sulfonyl) ethyl) oxy-] carbonyl] trimethylene] dipiperidine (No.2-2) — a polymer — receiving — 20wt(s)% — it added and considered as the solution of a photosensitive constituent. Spin spreading of this solution was carried out on the silicon wafer on 1000rpm and the conditions for 30 seconds, and it prebaked by heating for 1 minute at 110 degrees C. After irradiating ultraviolet rays at this paint film, it heated for 15 minutes at 110 degrees C, and postbake processing was performed. Furthermore, it was immersed in 2-methoxy ethyl acetate for 30 seconds, and this film was developed. It washed and dried by ethanol, thickness was measured, and the sensitivity curve was searched for. Consequently, it turned out by adding a base growth agent that sensibility improves also 4 times rather than the system under base growth agent un-existing. Moreover, after carrying out UV irradiation of the film which carried out spin spreading over the photo mask, the clear negative-mold image was obtained by washing of 2-methoxy ethyl acetate.

[Translation done.]